

# Thermoelectric properties of the brownmillerite oxide $\text{Ca}_{2-y}\text{La}_y\text{Co}_{2-x}\text{Al}_x\text{O}_5$

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We prepared the brownmillerite oxide  $\text{Ca}_{2-y}\text{La}_y\text{Co}_{2-x}\text{Al}_x\text{O}_5$ , and found that it was an n-type conductor. The thermopower and the resistivity of the single crystal are  $-90 \mu\text{V/K}$  and  $68 \text{ m}\Omega\text{cm}$  along the  $ab$  direction at 440 K, which suggest relatively good thermoelectrical properties, compared with other transition-metal oxides. Their temperature dependences are of activation type, and the activation energies are 0.2 eV for the resistivity and 0.04 eV for the thermopower. These energies differ by one order in magnitude, which implies that a polaron dominates the charge transport. A sign of the thermopower of the polycrystals changes from negative to positive at 500 K, indicating that holes are excited thermally to decrease the magnitude of thermopower.

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## I. INTRODUCTION

Thermoelectric materials, which convert heat into electricity and vice versa through the thermoelectric phenomena in solids, have recently attracted a renewed interest as a promising energy-conversion technology that is friendly to the environment. The conversion efficiency of a thermoelectric material is characterized by the figure of merit  $Z = S^2/\rho\kappa$ , where  $S$ ,  $\rho$  and  $\kappa$  are the thermopower, the resistivity, and the thermal conductivity, respectively.

Recently Terasaki *et al.*[1] found that a layered cobalt oxide  $\text{NaCo}_2\text{O}_4$  shows a large thermopower of  $100 \mu\text{V/K}$  and a low resistivity of  $200 \mu\Omega\text{cm}$  at room temperature, and they proposed that the strong correlation plays an important role in the enhancement of the thermoelectric properties. Based on this proposal, other layered cobalt oxides  $\text{Bi-Sr-Co-O}$ [2, 3] and  $\text{Ca-Co-O}$ [4, 5, 6] have been studied, and they are found to be potential thermoelectric materials as well as  $\text{NaCo}_2\text{O}_4$ . In particular, Funahashi *et al.*[6] reported the maximum of  $ZT$  is larger than 1.2 for  $\text{Ca-Co-O}$ , which means that the layered cobalt oxides might be the best group among all the thermoelectric materials.

These layered cobalt oxides are, however, all p-type materials, and an n-type cobalt oxide has not been found yet. Thermoelectric devices are made from a pair of p and n-type thermoelectric materials, and we tried to find an n-type cobalt oxide. The Co ion in  $\text{NaCo}_2\text{O}_4$  is at the center of an oxygen octahedron, and its average valence is +3.5 with the electron configuration of  $(3d)^{5.5}$ , which corresponds to 0.5 hole in the  $t_{2g}$  bands per Co site. In  $\text{NaCo}_2\text{O}_4$ , the octahedron is edge-shared, where the  $t_{2g}$  bands of Co  $3d$  directly overlap each other. By contrast, electrons doped in an insulating cobalt oxide

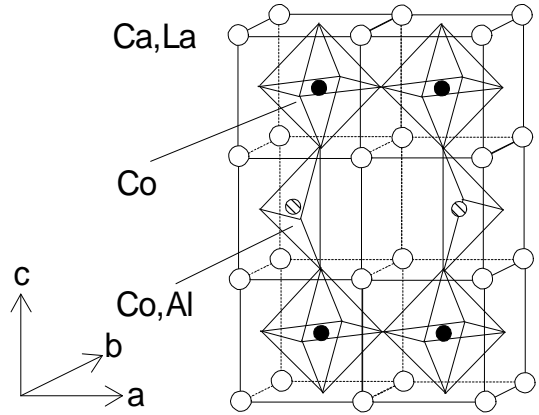


FIG. 1: Schematic view of the brownmillerite structure.

made of  $\text{Co}^{3+}$  will be in the  $e_g$  bands. Since the  $e_g$  bands are strongly hybridized with O  $2p$ , the conduction-band width is largest when the bonding angle of Co-O-Co is  $180^\circ$ . Thus a cobalt oxide in a corner-shared oxygen octahedron will be a good n-type conductor.

Accordingly we searched for a cobalt oxide in a corner-shared oxygen octahedron, and eventually found  $\text{Ca}_2(\text{Co,Al})_2\text{O}_5$ [7], which has a brownmillerite structure with  $\text{Co}^{3+}$ . The brownmillerite structure is schematically shown in Fig. 1. Big white circles represent Ca and La, black circles Co, shaded circles Al and Co. This structure is composed of an alternate stack of the  $\text{CoO}_2$  square lattice and the  $(\text{Co,Al})\text{O}$  chain along the  $c$  direction, and can be regarded as an oxide-deficient perovskite structure. In this paper we report on preparation of polycrystalline and single-crystal samples, and on measurements and analyses of their thermoelectric properties.

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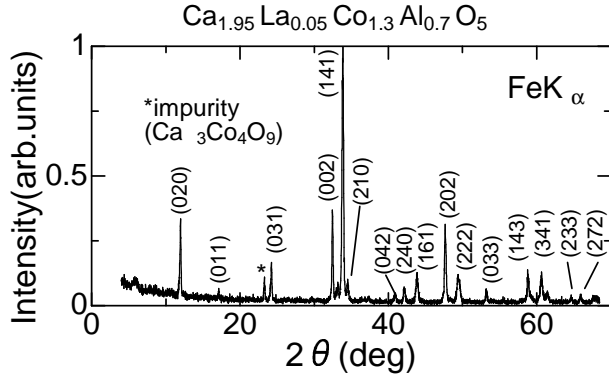


FIG. 2: X-ray diffraction pattern of  $\text{Ca}_{1.95}\text{La}_{0.05}\text{Co}_{1.3}\text{Al}_{0.7}\text{O}_5$ .

## II. EXPERIMENTAL

Polycrystalline samples of  $\text{Ca}_{2-y}\text{La}_y\text{CoAlO}_5$  ( $y = 0, 0.05, 0.1$  and  $0.15$ ) and  $\text{Ca}_{1.95}\text{La}_{0.05}\text{Co}_{2-x}\text{Al}_x\text{O}_5$  ( $x = 0.4, 0.5, 0.6$ , and  $0.7$ ) were prepared by a solid-state reaction. Stoichiometric amounts of  $\text{CaCO}_3$ ,  $\text{La}_2\text{O}_3$ ,  $\text{Co}_3\text{O}_4$  and  $\text{Al}_2\text{O}_3$  were mixed, and the mixture was calcined at  $900^\circ\text{C}$  for 12h in air. The product was finely ground, pressed into a pellet, and sintered at  $960^\circ\text{C}$  for 12h in air.

Single-crystal samples were prepared by a  $\text{Bi}_2\text{O}_3/\text{PbO}$  flux method.  $\text{Bi}_2\text{O}_3$ ,  $\text{PbO}$ ,  $\text{CaCO}_3$  and  $\text{Co}_3\text{O}_4$  powders were mixed with a cationic composition of  $\text{Bi}:\text{Pb}:\text{Ca}:\text{Co}=1.3:0.7:3:2$ , and was heated at  $1100^\circ\text{C}$  for 5h, and then slowly cooled down to  $700^\circ\text{C}$  at a rate of  $8^\circ\text{C}/\text{h}$  in air using an  $\text{Al}_2\text{O}_3$  crucible (Al was supplied from the crucible). The composition ratio of a single-crystal sample measured by energy dispersive X-ray analysis (EDX) is  $\text{Ca}:\text{Co}:\text{Al}=2:1.3:0.7$ .

The X-ray diffraction (XRD) of the sample was measured using a standard diffractometer with  $\text{Fe K}\alpha$  radiation as an X-ray source in the  $\theta - 2\theta$  scan mode. The resistivity was measured using a four-probe method, below room temperature in a liquid He cryostat, and above room temperature in an electric furnace. The thermopower was measured using a steady-state technique, below room temperature in a liquid He cryostat, and above room temperature in an electric furnace. A temperature gradient of  $1 \text{ K}/\text{cm}$  was generated by a small resistive heater pasted on one edge of a sample, and was monitored by a differential thermocouple made of copper-constantan below room temperature, and by that of platinum-rhodium above room temperature. The thermopower of the voltage leads was carefully subtracted. The thermal conductivity was measured from 30 to 280 K using a steady-state technique in a closed refrigerator pumped down to  $10^{-6}$  Torr. The temperature gradient was monitored using a differential thermocouple made of chromel-constantan.

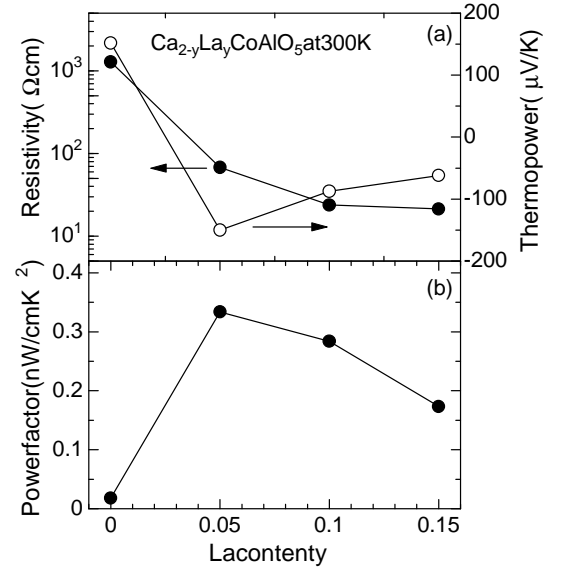


FIG. 3: (a) Resistivity and the thermopower of  $\text{Ca}_{2-y}\text{La}_y\text{CoAlO}_5$  at 300 K and (b) power factor of  $\text{Ca}_{2-y}\text{La}_y\text{CoAlO}_5$  at 300K.

## III. RESULTS AND DISCUSSION

Figure 2 shows an XRD pattern of a polycrystalline sample  $\text{Ca}_{1.95}\text{La}_{0.05}\text{Co}_{1.3}\text{Al}_{0.7}\text{O}_5$ . A small amount (at most 7%) of impurity phase (mainly  $\text{Ca}_3\text{Co}_4\text{O}_9$ ) [5] is seen, but almost all the peaks are indexed as the brownmillerite phase. The lattice parameters were obtained to be  $a = 5.28 \text{ \AA}$ ,  $b = 5.52 \text{ \AA}$ , and  $c = 14.66 \text{ \AA}$ , which is consistent with a 4-cycle X-ray diffraction of a single crystal. We will use the composition as the nominal composition in the present paper, though the real composition is different from the nominal composition. However, the difference is small within less than 10% accuracy: for example a nominal La [Al] content of 0.05 [0.5] corresponds to 0.053 [0.54] for the real composition at most. We further note that the impurity phase of  $\text{Ca}_3\text{Co}_4\text{O}_9$  shows positive and nearly temperature-independent thermopower above 100 K [5], which would not seriously affect the temperature and the composition dependences of  $\rho$  and  $S$ , or the discussion in the present paper.

Figure 3(a) shows  $\rho$  and  $S$  of polycrystalline  $\text{Ca}_{2-y}\text{La}_y\text{CoAlO}_5$  at room temperature. With increasing La content  $y$ ,  $\rho$  decreases systematically, and the sign of  $S$  changes from positive to negative. This indicates that the substitution of  $\text{La}^{3+}$  for  $\text{Ca}^{2+}$  supplies an electron. Figure 3(b) shows the power factor  $S^2/\rho$  corresponding to the data in Fig 2(a). The power factor takes a maximum at  $y=0.05$ , and accordingly we fix  $y$  to be 0.05 to see the Al-content dependence.

Figure 4(a) shows  $\rho$  of polycrystalline samples of  $\text{Ca}_{1.95}\text{La}_{0.05}\text{Co}_{2-x}\text{Al}_x\text{O}_5$ , together with the in-plane (parallel to the  $ab$  direction) and the out-of-plane (parallel to the  $c$  direction) resistivity of a single-crystal sample of  $\text{Ca}_2\text{Co}_{1.3}\text{Al}_{0.7}\text{O}_y$ . At 750 K, the magnitude of resis-

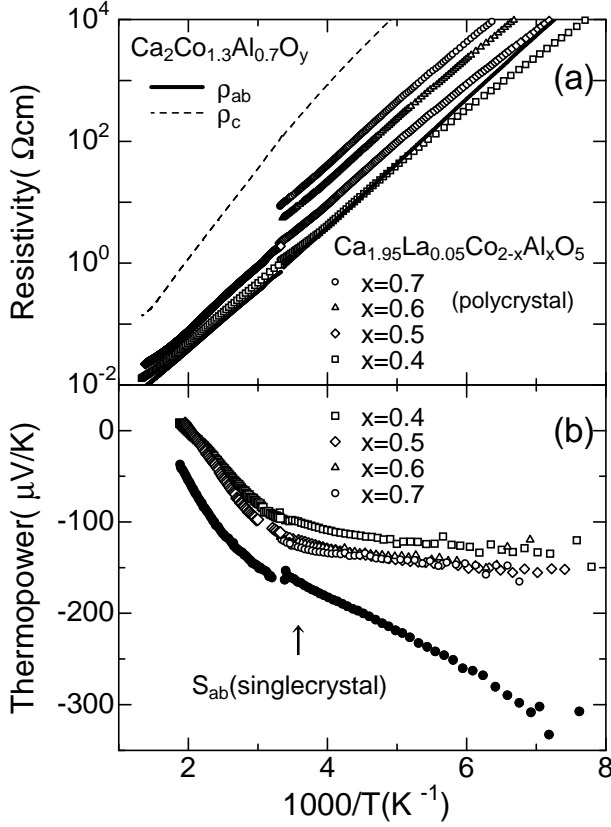


FIG. 4: (a) Resistivity and (b) thermopower of polycrystalline  $\text{Ca}_{1.95}\text{La}_{0.05}\text{Co}_{2-x}\text{Al}_x\text{O}_5$  and single-crystal  $\text{Ca}_2\text{Co}_{1.3}\text{Al}_{0.7}\text{O}_y$

tivity decreases down to 10-20 mΩcm for polycrystalline samples and the in-plane direction of the single crystals. This magnitude of resistivity is the lowest, to our knowledge, in brownmillerite oxides [8, 9]. The temperature dependence is described by an activation-type conduction, where the activation energy for resistivity ( $E_\rho$ ) is approximately 0.2 eV for all the samples. As for anisotropy, the out-of-plane resistivity is 100 times higher than that for the in-plane resistivity, implying that the layered structure is realized, as is expected from the brownmillerite phase. This means that the conduction path of a single crystal sample is two-dimensional, and the conduction path of the polycrystalline samples is mainly determined by the in-plane conduction paths. Then the resistivity of the polycrystalline samples is higher than the in-plane resistivity of the single crystal sample, while the temperature dependences are similar, as is also seen in the resistivity of high-temperature superconductors. The resistivity increases with increasing Al content  $x$ , which indicates that a Co ion is responsible for the electric conduction and an Al ion acts as an impurity. We should note that the brownmillerite structure was not synthesized for  $x \leq 0.4$ , which means that an Al ion is essential to stabilizing the brownmillerite structure at ambient pressure.

Figure 4(b) shows the thermopower of the prepared samples. The in-plane thermopower of the single-crystal sample is  $-150 \mu\text{V/K}$ , and that of polycrystalline samples is about  $-100 \mu\text{V/K}$  at 300 K. This means that the carrier concentration of the single-crystal sample is smaller than that of the polycrystalline samples, because no donor ion such as La is included in the single crystal. The source of the carrier is not clear at present, and the oxygen deficiency or a small inclusion of  $\text{Bi}^{3+}$  are possible candidates.

It should be emphasized that the magnitude and the temperature dependence of the thermopower of polycrystalline samples are nearly independent of  $x$ . Considering the  $x$  dependence of  $\rho$  and  $S$ , we can conclude that an Al ion acts as a scattering center (disorder) for electric conduction, although it stabilizes the brownmillerite structure at ambient pressure [7]. Consequently carriers are likely to conduct on  $\text{CoO}_2$  square lattice, not on the  $(\text{Co},\text{Al})\text{O}$  chain. Below 350 K, the temperature dependence of the thermopower is described by an activation-type conduction with the activation energy for thermopower ( $E_s$ ) of 0.01 eV for the polycrystalline samples, and 0.04 eV for the single-crystal sample.  $E_\rho (= 0.2 \text{ eV}) \gg E_s (= 0.01 - 0.04 \text{ eV})$  implies a polaron conduction, where  $E_\rho$  and  $E_s$  are described as  $E_\rho = E_F - E_c + W_H$  and  $E_s = E_F - E_c$  ( $E_c$ : the energy of bottom of conduction band,  $E_F$ : Fermi energy,  $W_H$ : hopping energy that contributes to the change of mobility by temperature)[10]. Such a material is useful for the high-temperature thermoelectric application [11], because a rapid decrease in  $\rho$  and a gradual decrease in  $S$  will occur with increasing temperature.

For the present material, however, the high temperature thermopower is quite small. Above 350 K it deviates from the activation type, and the sign of the thermopower of the polycrystalline samples changes from negative to positive at 500 K. A similar tendency was observed for the single-crystal sample, though a sign change was not yet seen below 550 K. As a result the thermoelectric performance rapidly decreases above 450 K. Very recently Ueno *et al.* have found a similar sign change of the thermopower in the brownmillerite Ca-Co-Al-O thin film [12].

Figure 5 shows the thermal conductivity of polycrystalline samples. The magnitude is about 20 mW/cmK, which is relatively low, possibly due to a solid solution of Co and Al. Using  $\kappa = 20 \text{ mW/cmK}$ , the figure of merit for  $x = 0.4$  is estimated to be of the order of  $10^{-6} \text{ K}^{-1}$  at 300 K, which is three orders of magnitude smaller than that of the conventional thermoelectric materials. By examining  $\rho$ ,  $S$  and  $\kappa$  individually, we find  $\rho$  is hopelessly high, while  $S$  and  $\kappa$  are comparable. This is due to the polaron conduction where the mobility is exponentially lowered with decreasing temperature.

Let us discuss the sign change of the thermopower at 500 K. We should note that the electronic states (and the crystal structure) of  $\text{Ca}_2(\text{Co},\text{Al})_2\text{O}_5$  resemble those of the cubic perovskite  $\text{LaCoO}_3$ , which is a p-type conductor at all temperatures[13]. Thus it is very likely that holes are

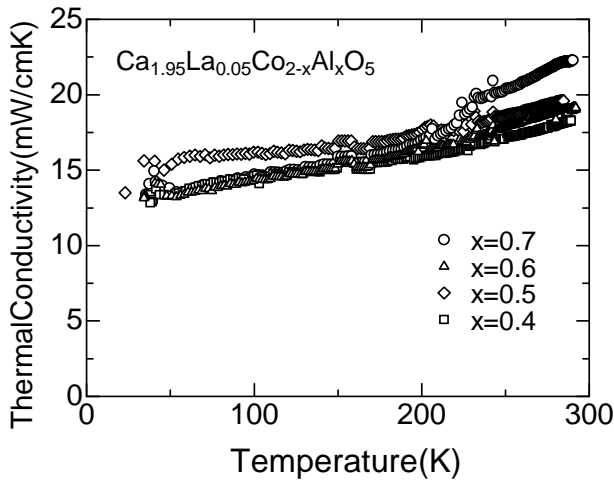


FIG. 5: Thermal conductivity of polycrystalline  $\text{Ca}_{1.95}\text{La}_{0.05}\text{Co}_{2-x}\text{Al}_x\text{O}_5$

thermally excited also in  $\text{Ca}_2(\text{Co},\text{Al})_2\text{O}_5$  at high temperature, which will compensate the doped electrons to decrease the magnitude of the thermopower. In general, the square lattice as seen in the brownmillerite is often symmetric to electron and hole doping (which is exact in the tight-binding approximation) [14, 15]. This means that electrons and holes are equally excited at high temper-

ature to give zero thermopower. Thus the electron-hole symmetry is unsuitable for good thermoelectrics, which might be the reason most of the perovskite related oxides are not good thermoelectric materials.

#### IV. SUMMARY

We successfully prepared an n-type Co oxide material for the first time, although the thermoelectric properties are not satisfactory. The figure of merit at 300 K is of the order of  $10^{-6} \text{ K}^{-1}$ , the low value of which comes from the high resistivity. The high resistivity is ascribed to the polaron conduction suggested by the fact that  $E_p$  is one order of magnitude larger than  $E_s$ . The sign change of the thermopower represents thermal excitation of holes at high temperatures. Thus it would be less advantageous to design an n-type thermoelectric material by using Co oxides with a corner-shared oxygen octahedron network.

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